

# Oxidation Kinetics of Carbon Fibers

Jae-Seung Roh<sup>▲</sup>

School of Advanced Materials and System Engineering, Kumoh National Institute of Technology 1, Yangho-dong, Gumi, Gyungbuk 730-701, Korea

<sup>▲</sup>e-mail: jsroh@kumoh.ac.kr

(Received May 12, 2004; Accepted November 25, 2004)

---

## Abstract

Isotropic pitch based carbon fibers were exposed to isothermal oxidation in carbon dioxide gas to study the activation kinetics under the temperature of 800~1100 °C. The kinetic equation  $f = 1 - \exp(-at^b)$  was introduced and the constant  $b$  was obtained in the range of 0.92~1.25. It was shown that the activated carbon fiber shows the highly specific surface area (SSA) when the constant  $b$  comes close to 1. The activation kinetics were evaluated by the reaction-controlling regime (RCR) according to changes of the apparent activation energy with changes of the conversion. It was observed that the activation energies increase from 47.6 to 51.2 kcal/mole with the conversion increasing from 0.2 to 0.8. It was found that the pores of the activated carbon fiber under the chemical reaction were developed well through the fiber.

**Keywords :** Activation, Kinetics, Mechanism, Isotropic carbon fiber

---

## 1. Introduction

The leading method to interpret the mechanism of pores development is measuring the specific surface area (SSA) of carbon material in each stage of activation. Most researchers explain the activation mechanism by a reaction-controlling regime after gaining activation energy when they measured the average rate of the overall activation of gasification reaction [1-6]. Oxidation reaction of general carbon materials is dominated by chemical reaction on the surface below 800 °C, and the activation energy shows the large value of 35~60 kcal/mole. At a higher temperature than that it is controlled by diffusion through internal pores, whose activation energy shows about half of the chemical reaction.

In addition to the active sites, the other factors affecting characteristics of oxidation reaction include microstructural characteristics related to the inhomogeneity taking place during the manufacture of the carbon materials [7, 8-11].

However, the report on interpretation of reaction mechanism of activated carbon materials via the data of activation energy with a tendency is hardly found. There are some reports only on granular carbon materials, but not on activated carbon fiber.

The purpose of this study is that the clear explanation on active reaction mechanism influencing pore development was tried by comparing the value of SSA measured by the BET method after gaining activation energy according to the conversion from each of oxidation rates. In this study, isotropic pitch based carbon fiber was used for activation with carbon dioxide.

## 2. Experiment

Isotropic pitch based carbon fibers were used as raw materials. The original fiber has been activated by isothermal oxidation in the horizontal tube reactor at 800 °C, 900 °C, 1,000 °C, and 1,100 °C. Burn-off was calculated by dividing the weight loss after activation by original weight of sample. The measurement of SSA of activated carbon fibers is the same as reported earlier [12].

In this experiment, carbon dioxide was used for oxidatant (0.4 L/min). It is well known that the carbon dioxide delays the reaction by formation of the intermediate products during the reaction and the regular reaction takes place in active sites [13, 14]. Besides, carbon material activated by carbon dioxide shows higher SSA than the one by other oxidatants [15, 16]. Therefore, activated carbon fiber which shows high SSA after activation reaction is expected to obtain. The slow reaction rate is considered to act as an advantage to adjustment of the reaction rate as well.

## 3. Results and Discussion

### 3.1. Activation reaction and SSA

Fig. 1 represents the relation between the weight changes of the original fiber in carbon dioxide and reaction time. As the temperature of oxidation reaction increased, the time for weight loss rapidly decreased.

Table 1 shows the SSA values of activated fibers with a weight loss from 40% to 60%. Although there is a difference

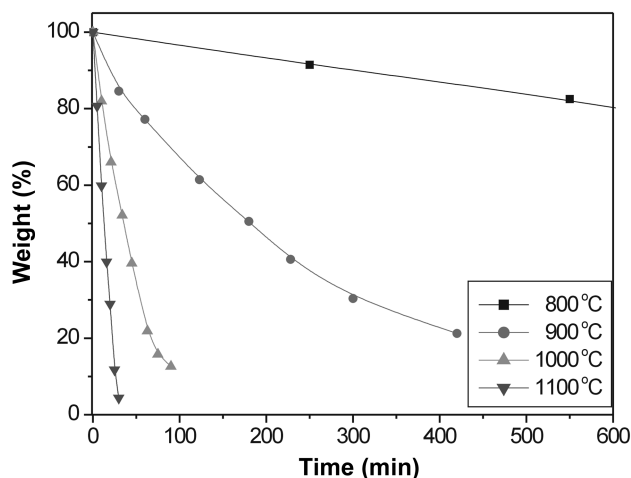


Fig. 1. Weight changes as a function of oxidation time and temperature in carbon dioxide gas.

Table 1. Specific surface areas (SSAs) of activated carbon fibers (ACFs)

Temperature (°C)	Burn-off (%)	SSA (m <sup>2</sup> /g)
800	27	970
	47	1,825
900	49	3,072
	59	3,495
1000	48	2,236
	60	3,614
1100	40	1,712
	60	2,049

according to reaction temperatures and weight loss, it was appeared that all oxidized fibers are excellent as activated carbon fibers. It is believed that pores well developed in activated fiber, and most of them are micropores as reported earlier [17, 14, 18-21].

Considering the fact that the SSA is different depending on various reacting conditions, activation mechanisms are expected to be different depending on reaction conditions.

### 3.2. Kinetic equation

Conversion  $f$  can be expressed  $f = 1 - W/W_0$ . Here,  $W_0$  is the initial weight of reactants, and  $W$  is the weight of reactants after reaction. Moreover, the kinetic equation  $f = 1 - \exp(-at^b)$  was suggested by Kasaoka [9]. Here,  $t$  is the reacting time, and  $a$  and  $b$  are constants. Constants  $a$  and  $b$  can be obtained by the least square method from the  $f-t$  graphs. Therefore, the data  $f-t$  can be to have expressed simplified to a vertical line in a  $Y = \ln a + bX$ ,  $Y = \ln[-\ln(1-f)]$  and  $X = \ln t$  here. Rate constant  $k$  with increasing conversion 0.2 to 0.8 was calculated from  $k(f) = a^{1/b} b [-\ln(1-f)]^{(b-1)/b}$ . The detail interpretation for the oxidation rate equation was reported

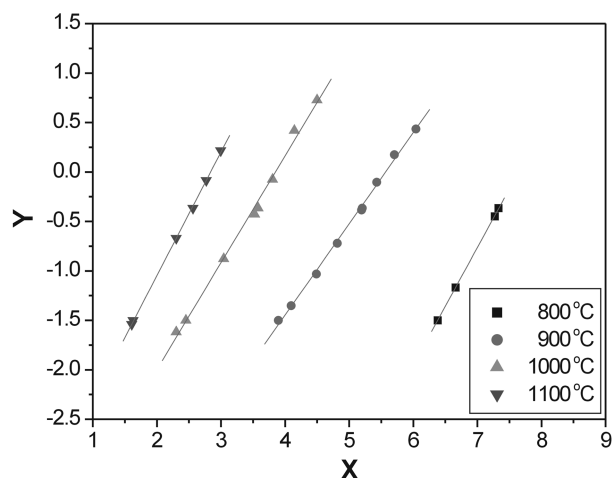


Fig. 2.  $Y-X$  plots from  $Y = \ln a + bX$  of isotropic carbon fiber.

earlier [22].

Fig. 2 presents the results which were calculated via  $Y = \ln a + bX$ . In all reacting temperatures, each reaction point obviously stays in the lines of  $Y-X$  graphs. Optimization of lines in graphs was tried between reaction paths from 0.2 to 0.8 of the conversion. A correlation coefficient ( $r$ ) of optimized lines was more than 0.997. Moreover,  $\ln a$  and  $b$  obtained from  $Y = \ln a + bX$  and an average rate constant  $K$  are summarized in Table 2. The average rate constant was gained by the average of rate constant from each conversion.

The important meaning of the equation  $Y = \ln a + bX$  is the  $b$  value [9]. If it is  $0 < b \leq 1$ , activation rate decreases as a function of the activation reaction proceeds. If it is  $b = 1$ , activation rate is generally steady during the whole activation, and activation reaction is the stage controlled by the continuous chemical reaction.

As seen in Table 2, constant  $b$  value of fiber is gained between 0.9226-1.2514. In the case that  $b$  value of fiber gets closer to 1 (900 °C and 1000 °C), it seems that steady activation reaction in active sites takes place by the chemical reaction. Also, when compared with the SSA in Table 1 and  $b$  value in Table 2, it is clear that the SSA of the activated fiber is much larger when  $b$  value gets closer to 1.

Therefore, it is believed that the constant  $b$  gets closer to

Table 2.  $\ln a$ ,  $b$  and  $K$  calculated by  $Y = \ln a + bX$

Temperature (°C)	$\ln a$	$b$	$K^*$	$r^\#$
800	-9.0804	1.1180	0.00050	1.000
900	-5.1373	0.9226	0.00373	0.999
1000	-4.1597	1.0806	0.02227	0.997
1100	-3.5513	1.2514	0.07077	1.000

\*Average rate constant.

#Correlation coefficient.

**Table 3.** Reaction rates as a function of conversion

Conversion ( <i>f</i> )	Reaction rate ( <i>k</i> )			
	800 °C	900 °C	1000 °C	1100 °C
0.2	0.00045	0.00399	0.02058	0.05420
0.5	0.00054	0.00363	0.02239	0.06806
0.8	-	0.00338	0.02385	0.08082

1, then SSA of the activated fiber is considered to become larger.

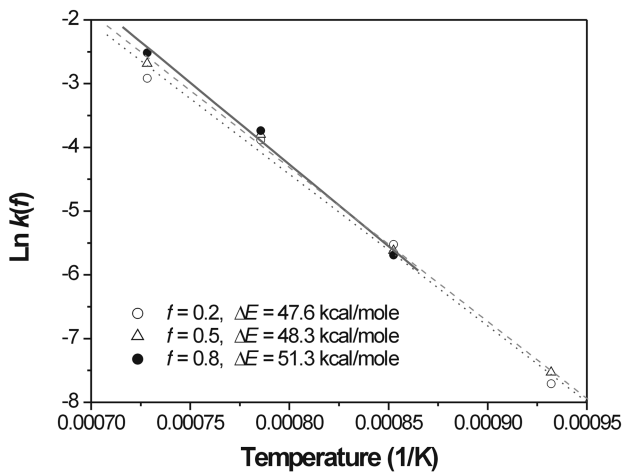
### 3.3. Activation reaction mechanism

#### 3.3.1. activation energy

Rate constant values according to the conversion at each activation temperature are summarized in Table 3. In most experimental conditions except for the case in which fiber was activated at 900 °C, the reaction rate increased as the conversion increased. Also, the values of rate constant at the conversion 0.5 show similar value with average rate constant. It means the kinetic equation functionally expressed with constant *a* and *b* was adequate to the reaction analysis for this study [22].

Fig. 3 shows Arrhenius graph which was obtained from rate constants. Activation energy in the Arrhenius graph shows 47.6~51.3 kcal/mole. Therefore it is clear that activation reaction of the isotropic pitch based carbon fiber is dominated by the chemical reaction on the basis of the concept of the reaction-controlling regime [1-6].

Gasification of carbon materials has a close relationship with structural defaults, which is pores. In this study, there are already many pores in the original fiber, because the original fiber was poorly oriented with tiny crystallites [16, 23, 24]. It could be supposed that the more structural defaults in original fibers, the faster the gasification. However, it does not necessarily mean that the gasification rate is

**Fig. 3.** Changes of the Arrhenius plot as a function of conversion.

related to the value of activation energy as reported elsewhere [2, 25, 26]. Therefore, the interpretation of reaction mechanism by using activation energy should be based upon development procedure of pores.

Out of several models for interpreting reaction mechanism of gasification of carbon materials using activation energy, Progressive - Conversion Model (PCM) and Shrinking - Core Model (SCM) are well known [10]. Activation energy of PCM shows a larger value more than 35 kcal/mole. It is applied to activation reaction of small particles and to activation reaction in the low temperature, in whose case the diffusion rate is large and reaction rate is controlled by the chemical reaction. SCM is relatively applied to activating process of large particles at the high temperature since it has only half of activation energy of PCM. In this case, reaction is controlled by diffusion control in pores, and activation proceeds from the surface of large particles toward the center.

Considering the value of activation energy, PCM can be applied to fiber which was used in this study. Original fiber has small crystallites and low density, finally giving more active sites for reaction with many pores already inside as well. Therefore, if pores on the fiber surface are opened in the initial stages of activation, it is possible for active sites existing inside the fiber to chemically react. At this point, it seems that pore development into the fiber from the fiber surface can take place easily since diffusion rate of products and reacting materials through pores are quite large.

Energetic activation in the internal parts of fiber was reported by Hashimoto who examined the procedures of development of pores [27]. He measured the density of carbon materials according to the conversion and discovered a difference between the external conversion and the internal conversion. He reported that the high SSA after activation is due to the fact that the internal conversion is larger than the external conversion. Consequently, it seems that activation reaction mainly takes place at the active sites of internal parts of the fiber, which presents the high SSA after activation.

#### 3.3.2. Changes of activation energy

Changes of activation energy according to the conversion are presented in Fig. 4. Activation energy of fiber increased from 47.6 to 51.3 kcal/mole with increasing conversion. This means activation reaction is more controlled by the chemical reaction as the conversion increases.

The process of pore development by activation reaction needs diffusion of reaction products through pores and reacting gas as well as chemical reaction of carbon atoms. Therefore, the number of active sites are proportional to the number of carbon atoms at the crystallite-ends. If the crystallites are small, there are more active sites.

Since pores are created or enlarged by the removal of carbon atoms existing in the active sites, the sizes of

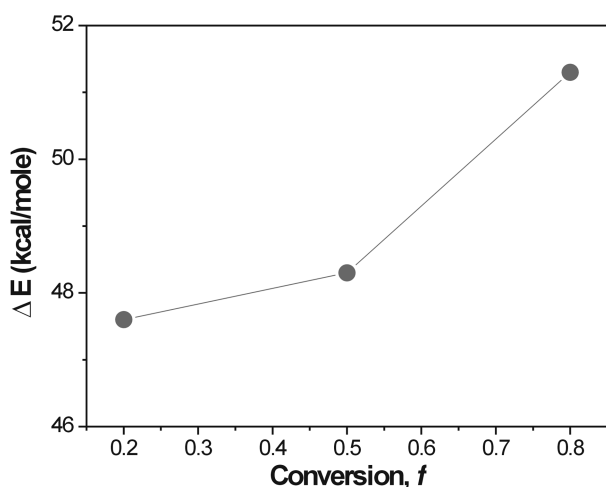


Fig. 4. Changes of the activation energy as a function of conversion.

crystallites will decrease as the pores develop. After all, the number of active sites increase as the crystallites sizes decrease. This means that the number of active sites exposed to the crystallite-ends increase as activation reaction proceeds. Therefore, the reason that activation energy increases as the conversion is that the number of active sites increases as pores develop inside the fiber.

### 3.3.3. Relation with constant $b$

Pore developments to reacting temperatures can be explained from the constant  $b$  value of  $Y = \ln a + bX$  in 3.2 paragraph based on activation energy.  $b$  value of fiber was 1.1180 gained at 800 °C, fell to 0.9226 at 900 °C, and increased to 1.0806 at 1000 °C and to 1.2514 at 1100 °C. This mechanism of pore development of fiber is thought to be quite complicated.

The constant  $b$  of fiber activated at 900 °C showed a value smaller than 1, and increased at a higher temperature than 900 °C. The tendency of active sites decreasing at 900 °C is possibly explained by the activation process causing effect of heat treatment to the fiber.

The effect of heat treatment during activation for the carbon materials has been reported by many researchers [28-31]. Many researchers reported that carbon fiber with high SSA after activation was partially carbonized due to insufficient heat treatment while manufacturing. As such carbonization reaction could take place during activation at a high temperature. Therefore, the existing crystallites inside the fiber can grow by heat treatment at a high temperature. If the crystallite growth inside the fiber takes place, the number of overall active sites in all the fiber will decrease. However, the sizes should still be tiny even though crystallites will ever grow due to effect of heat treatment after activation since the crystallite sizes of the original fiber are so tiny (around 1 nm) [15, 17, 20, 30]. Therefore, there would be no

problem in pore development during activation, and the activated fiber still have as many active sites.

It is considered that the reason active sites increased at over 1000 °C is that the activation rate is faster than the growth rate of crystallites because of the effect of heat treatment. If gasification rate is faster than the growth rate of crystallites, pores could progress inwards the fiber for the increase of the number of active sites per unit weight, finally showing high SSA.

Also, it is considered that the constant  $b$  increases more at 1100 °C than lower temperature is that the crystallite sizes decrease quickly due to fast gasification. It is believed that the fast decrease of crystallite sizes at such a high temperature has the same effect as the excessive enlargement of the initially developed pores around the fiber surface. Thus, the SSA shows a smaller value than the fiber activated at lower temperatures.

## 4. Conclusion

Isotropic pitch based carbon fibers were exposed in carbon dioxide. After activation energy was gained according to the conversion at each reacting temperature, the value of SSA was compared, and the reaction mechanism of activation affecting development of pores of carbon fibers was examined to get the results like the following.

Activation energy of isotropic fiber increases from 47.6 to 51.3 kcal/mole with increasing conversion from 0.2 to 0.8. Therefore, it is believed that the reason isotropic carbon fiber can be manufactured as the activated carbon fiber, which has high SSA (over 3,000 m<sup>2</sup>/g) after activation, is that the activation reaction is controlled by the chemical reaction during the whole process.

The constant  $b$  of the reaction equation used in this study is considered very useful. It is observed that as constant  $b$  gets closer to 1, the SSA gets higher. Therefore, it is clear that SSA of the fiber activated at a certain temperature increase when steady activation reaction in active sites take place by the chemical reaction, that is,  $b$  value gets closer to 1.

## References

- [1] Lafdi, K.; Bonnamy, S.; Oberlin, A. *Carbon* **1992**, *30*, 533.
- [2] Ismail, M. K. *Carbon* **1991**, *29*, 777.
- [3] Li, T.; Zheng, X. *Carbon* **1995**, *33*, 469.
- [4] Tanabe, Y.; Utsunomiya, M.; Ishibashi, M.; Kyotani, T.; Kaburagi, Y.; Yasuda, E. *Carbon* **2002**, *40*, 1.
- [5] Matsumura, Y.; Xu, X.; Antal, M. J. Jr. *Carbon* **1997**, *35*, 819.
- [6] Tomlinson, J. B.; Freeman, J. J.; Sing, S. W.; Theocharis,

- C. R. *Carbon* **1995**, *33*, 789.
- [7] Mahajan, O. P.; Yarzab R.; Walker Jr. P. L. *Fuel* **1978**, *57*, 643.
- [8] Sanchez, A. R.; Elguezabal, A. A.; Torre Saenz, L. L. *Carbon* **2001**, *39*, 1367.
- [9] Kasaoka, S.; Sakata, Y.; Kayano, S.; Masuoka, Y. *Int. Chem. Eng.* **1983**, *23*, 477.
- [10] Hu, Y. Q.; Nikzat, H.; Nawata, M.; Kobayashi, N.; Hasatani, M. *Fuel* **2001**, *80*, 2111.
- [11] Rafsanjani, H. H.; Jashidi, E.; Rostam-Abadi, M. *Carbon* **2002**, *40*, 1167.
- [12] Roh, J. S.; Suhr, D. S. *Carbon Science* **2004**, *5*, 51.
- [13] Marsh, H.; Reinoso, F. R. *Science of Carbon Materials*; Universidad de Alicante, Alfredo Candela, **2000**, 379.
- [14] Mattson, J. S.; Mark, H. B. Jr, *Activated Carbon*; Marcel Dekker, New York, 1971, p 20.
- [15] Yoshizawa, N.; Yamada, Y.; Shiraishi, M. *J. of Mater. Sci.* **1998**, *33*, 199.
- [16] Sha, X. Z.; Kyotani, T.; Tomita, A. *Fuel* **1990**, *69*, 1564.
- [17] Kaneko, K.; Ishii, C.; Ruike, M.; Kuwabara, H. *Carbon* **1992**, *30*, 1075.
- [18] Shim, H. S.; Hurt, R. *In Proceeding 23rd Biennial Conference in Carbon* **1997**, 438.
- [19] Chang, Q.; Liu, T.; Cal, X. *In Proceeding 22nd Biennial Conference in Carbon* **1995**, 514.
- [20] Mays, T.; Howell, J.; King, L.; McEnaney, B.; Edie, D. *In Proceeding 22nd Biennial Conference in Carbon* **1995**, 510.
- [21] Fryer, J. R. *Carbon* **1981**, *19*, 431.
- [22] Roh, J. S. *Carbon Science* **2004**, *5*, 27
- [23] Montes-Moran, M. A.; Young, R. J. *Carbon* **2002**, *40*, 845.
- [24] Shioya, M.; Ojima, T.; Yamashita, J. *Carbon* **2001**, *39*, 1869.
- [25] Ismail, M. K.; Hurley, W. C. *Carbon* **1992**, *30*, 419.
- [26] Dami, T. L.; Manocha, L. M.; Bahl, O. P. *Carbon* **1991**, *29*, 51.
- [27] Hashimoto, K.; Imai, I. *Ameri. Cera. Soci.* **1978**, *18*, 72.
- [28] Kamegawa, K.; Nishikubo, K.; Yoshida, H. *Carbon* **1998**, *36*, 433.
- [29] Sharma, A.; Kyotani, T.; Tomita, A. *Fuel* **1999**, *78*, 1203.
- [30] Yoshizawa, N.; Maruyama, K.; Yamada, Y.; Zielinska-Blajet, M. *Fuel* **2000**, *79*, 1461.
- [31] Gondy, D.; Ehrburger, P. *Carbon* **1997**, *35*, 1745.